A Comprehensive Review on The Ballistic and Environmental Performance Of ADN, AN, And GN-Based Green Composite Solid Propellants

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***Abstract*—Solid propellants serve as the core energetic foundation for modern orbital launch vehicles and tactical missile defence systems. Traditional formulations depend on Ammonium Perchlorate (AP) chemistry, which presents severe environmental challenges via toxic hydrochloric acid (HCl) exhaust signatures and high combustion instability. This review paper systematically evaluates the emerging paradigm of "green" rocket propulsion by analysing the fundamental ballistic, thermochemical, and material characteristics of alternative oxidizers: Ammonium Dinitramide (ADN), Ammonium Nitrate (AN), and Guanidine Nitrate (GN), bound within a Hydroxyl-Terminated Polybutadiene (HTPB) polymer matrix. Through a comparative synthesis of existing experimental literature, molecular dynamics simulations, and thermochemical trends, this study evaluates critical parameters including specific impulse (Isp), pressure exponents (n), phase transformation mechanics, and ignition temperatures. Furthermore, we outline persistent operational risks such as acoustic combustion instability, condensed-phase slag formation, and structural grain micro-cracking. This provides a roadmap for optimizing alternative grain geometries and structural binder modifiers to accelerate the deployment of chlorine-free, high-efficiency solid rocket motors.**

I. INTRODUCTION

Solid rocket propulsion represents one of the most mature and operationally dependable fields within aerospace engineering. Unlike liquid bi-propellant architectures that mandate intricate turbopumps, valving networks, and cryogenic storage, a solid composite propellant functions as an integrated, self-contained energy unit where the fuel, oxidizer, and energetic catalysts are cast into a single, structurally stable solid matrix known as the grain. Once thermal ignition is started across the exposed internal port surface, the chemical reaction progresses predictably along a deflagration wave front. The high-temperature, high-pressure gaseous combustion products are subsequently choked and expanded through a convergent-divergent de Laval nozzle, translating thermal energy into kinetic thrust via gas dynamic expansion in accordance with Newton's Third Law of Motion.

The historical trajectory of solid energetics dates back to primitive black powder formulations (consisting of potassium nitrate, charcoal, and sulphur) utilized in ancient Chinese fire arrows. However, these early mixtures lacked the volumetric energy density, mechanical plasticity, and burn predictability necessary for modern aerospace systems. Decades of mid-20th-century chemical synthesis led to the development of highly filled Ammonium Perchlorate Composite Propellants (APCP). While APCP delivers excellent performance and mechanical stability, its atmospheric exhaust releases significant quantities of chlorine-based chemical species, inducing severe localized ozone depletion and acid rain.

Consequently, modern propulsion research is heavily focused on green alternatives that eliminate halogenated chemical components without compromising ballistic efficiency.

1.1. Fundamental Ballistic Requirements

The design of any solid composite propellant involves optimizing coupled thermochemical and mechanical parameters:

- Specific Impulse:

An absolute metric of a propellant's thermodynamic efficiency, representing thrust generated per unit mass flow rate of the ejected.

- Burning Rate (r) and Saint-Robert's Law:

The linear recession speed of the burning propellant surface normal to the grain orientation is characteristically governed by Saint-Robert's empirical law:

r = a*pn

Where a is the temperature-dependent burning rate coefficient, p is the internal chamber pressure, and n is the pressure sensitivity exponent. For safe, non-catastrophic motor operations, the pressure exponent must be tightly controlled ($n < 0.6$). If $n > 1$, any minor fluctuation in chamber pressure will trigger an exponential acceleration of the burning rate, resulting in structural over-pressurization and catastrophic motor casing rupture.

- Mechanical Integrity and Viscoelasticity:

The propellant grain is not merely an energetic supply; it functions as a critical structural element within the motor casing. During ignition transients, it experiences extreme pressure gradients (dP/dt) and intense thermal shocks. Any internal micro-voids, binder-oxidizer debonding, or cracking drastically increases the instantaneous burning surface area (A_b), shifting the mass generation rate balance out of equilibrium and causing catastrophic failure.

II. COMPREHENSIVE LITERATURE SURVEY

The foundational science of interior ballistics, multi-phase fluid dynamics, and energetic crystals is thoroughly documented across contemporary literature:

Fabignon et al. [1, 6] provided an extensive computational framework mapping the coupled multi-phase flows and internal ballistic phenomena within solid rocket motor chambers. Their research emphasizes that modeling the interaction between the gas phase and condensed-phase droplets is critical for predicting localized acoustic attenuations and nozzle thermal erosion profiles.

Focusing on conventional AP/HTPB microscopic interactions, Sun et al. [2, 7] implemented a gas-solid-coupled sandwich combustion simulation to investigate oxidizer particle packing distributions. Their findings established that migrating from a monomodal large-particle configuration to a bimodal distribution rich in fine-grain AP (shifting the flame structure from purely diffusion-dominated to a fast, premixed flame regime) escalated the linear burning rate from 0.9 cm/s to 2.7 cm/s at identical chamber pressures. Sun and Wang [15] expanded on this by proving that optimal packing topologies minimize unrefined matrix slurry viscosity, enhancing the structural castability of complex grain geometries.

To eliminate the toxic halogen signatures intrinsic to AP chemistry, alternative oxidizers have undergone thorough evaluation. Phondekar and Biswas [3, 8] investigated the thermal decomposition kinetics of Ammonium Nitrate (AN). While AN represents an inexpensive and clean alternative, it suffers from severe polymorphic volume changes during thermal cycling (specifically the IV < >III phase transition at 32.3^{C}). Their experimental work demonstrated that the inclusion of transition metal oxide catalysts, specifically ferric oxide (Fe_2O_3) and manganese dioxide (MnO_2), successfully locks the crystal structure, suppressing phase transitions while accelerating low-temperature decomposition. Phondekar and Biswas [13] confirmed that Phase-Stabilized Ammonium Nitrate (PSAN) effectively lowers the global activation energy barrier, unlocking a steady release of non-toxic gaseous products.

Simultaneously, Ammonium Dinitramide (ADN) has emerged as a premier high-energy green oxidizer. Kore and Vashishtha [4, 11] conducted a comprehensive review on ADN's physicochemical behavior, identifying its high oxygen balance and chlorine-free exhaust path. They noted that while ADN provides superior energetic potential, challenges regarding its severe hygroscopicity must be resolved using surface co-crystallization or polymer encapsulation techniques. Kore and Vashishtha [14] further detailed this via computational fluid dynamics (CFD), mapping the unique "dark zone" and "luminous flame" profiles above burning ADN/HTPB interfaces, highlighting that precise interface chemistry control is mandatory to manage high heat release rates.

To overcome the reduced burning rates characteristic of green oxidizers, nano-energetics have been

introduced. Zhang et al. [12] demonstrated that replacing traditional micron-sized aluminum particles with nano-scale aluminum significantly truncates ignition delay parameters and enhances localized flame propagation due to the exponentially expanded specific surface area. To improve the processing safety of these sensitive materials, Zhang et al. [10] mapped detailed protocols for encapsulating ADN particles within protective polymer skins, improving chemical compatibility with highly filled polyurethane binders.
From a system-level engineering perspective, Alemayehu and Solomon [5] detailed the strict internal ballistic workflow required to map total impulse definitions into specific internal core grain geometry dimensions. Finally, Wang et al. [9] utilized advanced finite element method (FEM) techniques to capture the non-linear viscoelastic stress-strain tensors experienced by highly filled composite grains, validating that structural safety factors require tightly coupled thermal-mechanical grid modeling.

III. COMPARATIVE SYNTHESIS OF GREEN OXIDIZERS

To evaluate the viability of replacing Ammonium Perchlorate (AP) with eco-friendly alternatives like Ammonium Dinitramide (ADN), Ammonium Nitrate (AN), and Guanidine Nitrate (GN), their baseline thermochemical and ballistic properties must be directly contrasted.

3.1. Thermodynamic Performance Comparison

- Ammonium Perchlorate (AP):

Delivers excellent energetic performance with a theoretical specific impulse (Isp) ranging from 260 s to 270 s when bound with HTPB. However, its combustion releases approximately 15-20 mol % of toxic hydrogen chloride (HCl) gas, creating highly corrosive, reflective exhaust plumes [3, 11].

- Ammonium Dinitramide (ADN):

Represents the highest energy alternative. Due to its superior oxygen balance (+25.8 %), ADN-based propellants achieve theoretical Isp values exceeding 275 s, outperforming traditional APCP formulations. It yields entirely non-toxic exhaust products (N_2, H_2O, and CO_2) [4].

- Ammonium Nitrate (AN):

Although incredibly cost-effective and environmentally clean, AN suffers from a low energy density and a low Isp (210-220 s). Its low burning rate coefficient requires intense catalytic modification [13].

- Guanidine Nitrate (GN):

Exhibits exceptionally high thermal stability and a low flame temperature, which reduces nozzle throat erosion. However, its low burning rate restricts its standalone application to gas generators or low-thrust auxiliary rocket units.

3.2. Quantitative Technical Baseline Matrix

The following table synthesizes the baseline performance, chemical characteristics, and operational parameters of conventional vs. green oxidizer matrices derived from the consolidated literature:

Oxidizer Candidate	Formula	Theoretical Max Isp (s)	Typical Pressure Exponent (n)	Primary Technical Challenge	Environmental Profile
Ammonium Perchlorate (AP) [2, 7]	NH_4ClO_4	260 – 270	0.30–0.45	Hydrochloric acid (HCl) exhaust signatures	Highly toxic; induces acid rain and ozone degradation
Ammonium Dinitramide (ADN) [4, 10]	$NH_4N(NO_2)_2$	275 – 285	0.55–0.70	Extreme hygroscopicity; high pressure sensitivity	Clean; zero chlorine output; low infrared signature
Ammonium Nitrate (AN) [3, 13]	NH_4NO_3	210 – 220	0.40–0.55	Volumetric crystalline phase transitions	Fully eco-friendly; non-toxic; highly sustainable

Guanidine Nitrate (GN) [1,5]	$C(NH_2)_3NO_3$	190 – 210	0.35–0.50	Low linear burning rate; difficult ignition characteristics	Low toxicity; produces clean, low-molecular-weight gases

IV. ANALYTICAL EVALUATION OF CRITICAL OPERATIONAL RISKS

4.1. Acoustic Combustion Instability

Combustion instability remains one of the most critical risks in solid rocket motor design [1]. This phenomenon stems from a positive feedback loop where acoustic pressure waves inside the motor chamber couple with the mass-burning response of the propellant grain. If the propellant's chemical response function matches the internal acoustic modes of the chamber geometry, localized pressure fluctuations amplify exponentially.

In ADN-based formulations, this risk is heightened by the oxidizer's high-pressure exponent ($n > 0.7$) [11]. Any minor acoustic pressure spike drastically accelerates the localized regression rate, creating rapid mass-flow fluctuations that can trigger structural motor failure.

4.2. Condensed-Phase Slag Accumulation

When metallic fuels like micron-sized aluminum are added to composite propellants to boost energetic output, the metal particles melt and coalesce at the burning surface, forming large droplets of molten aluminum/aluminum oxide (Al_2O_3). As the gas stream carries these heavy droplets toward the nozzle, they cannot accelerate at the same rate as the expanding gas phase.

This velocity lag creates two-phase flow losses that penalize specific impulse [6]. Furthermore, in spin-stabilized or forward-tapered motors, these molten residues pool in the aft-dome cavity surrounding the convergent nozzle section. This accumulated slag adds dead weight, degrades thermal insulation, and can induce asymmetric thrust tracking if ejected unevenly through the throat.

4.3. Thermal Stress and Viscoelastic Failure

Throughout its operational life, a solid propellant grain undergoes significant thermal cycling during storage, transport, and eventual ignition. Because the polymer binder (such as HTPB or HTPE) exhibits non-linear viscoelastic properties, it exhibits a time- and temperature-dependent stress response [9].

During the rapid ignition transient, the internal chamber pressure climbs from atmospheric to several megapascals in milliseconds, placing the cold propellant grain under severe tensile and shear strains. If the thermal expansion profiles of the binder and solid oxidizer crystals are mismatched, micro-cracks propagate along the grain boundaries. These hidden structural failures lead to an uncontrolled expansion of the internal port surface area during firing, resulting in unpredictable pressure spikes that can cause catastrophic motor casing failure.

V. ENGINEERING ADVANCED GRAIN STRUCTURES AND MANUFACTURING HORIZONS

5.1. Geometry Optimization Strategies

To regulate thrust without complex throttling systems, engineers alter the internal cross-sectional geometry (port area) of the propellant grain [5]. The burning surface profile directly dictates the internal ballistics over time.

- Cylindrical Bore (Progressive):

As the central burn port expands radially outward, the total burning surface area continuously increases, generating a progressive thrust-time profile.

- Star Grain (Neutral):

By balancing the regression of the star points against the flattening of the star valleys, the total burning surface area remains relatively constant throughout the burn duration.

- Finocyl Geometry (Regressive/Dual-Thrust):

Combines longitudinal slots with a radial star pattern. This design delivers a high initial surface area for maximum launch thrust, followed by a controlled decrease in surface area to limit structural aerodynamic loading as the vehicle accelerates through the atmosphere.

5.2. Advanced Manufacturing: Additive Manufacturing (3D Printing)

Traditional solid propellant manufacturing involves a complex casting and curing workflow: the energetic slurry is mixed, poured into a mould around a physical mandrel, and held at elevated temperatures for several days. This process severely limits the geometric complexity of the internal port, preventing the realization of highly optimized, non-axisymmetric grain profiles.

The integration of Additive Manufacturing (AM), specifically continuous screw extrusion 3D printing and stereolithography (SLA), represents a major paradigm shift in solid propulsion. 3D printing allows engineers to manufacture complex, functionally graded propellant grains where the oxidizer-to-fuel ratio varies continuously across the radial profile. By precisely controlling the local layer composition, a motor can be printed to transition smoothly from a high-energy booster formulation near the core to a cooler, case-bonding insulation layer near the outer wall. This eliminates structural interfaces prone to debonding while enabling precise control over the thrust-time curve to a degree impossible with traditional casting methods.

VI. FUTURE DEVELOPMENT HORIZONE

To enable the widespread adoption of green composite solid propellants, targeted research must address the following key performance and handling bottlenecks:

1. Hygroscopicity Mitigation via Co-Crystallization:

The industrial scaling of Ammonium Dinitramide (ADN) is currently constrained by its high affinity for atmospheric moisture, which degrades both its chemical purity and its mechanical bonding with polymer binders. Future research must prioritize the synthesis of non-hygroscopic ADN co-crystals, partnering the oxidizer molecule with stabilizing co-formers like urea or cytosine to shield it from moisture absorption without compromising its energy density.

2. Energetic Binder Integration:

Replacing inert binders like HTPB with energetic polymers such as Glycidyl Azide Polymer (GAP) or Hydroxyl-Terminated Polyether (HTPE) offers a clear path to high-performance green propulsion. These advanced binders contain energetic azido or ether functional groups within their molecular backbone, contributing positive heat of formation to the global combustion process and maximizing specific impulse even when paired with lower-energy oxidizers like Phase-Stabilized Ammonium Nitrate (PSAN).

3. Nano-Catalyst Customization:

To overcome the low linear burning rates and high-pressure exponents characteristic of green propellants, future formulations must leverage tailored nano-composite catalysts. Transitioning from raw metal oxides to structurally engineered core-shell nano-particles (e.g., $CuO\text{-}Fe_2O_3$ clusters) can safely lower pressure exponents ($n < 0.4$), ensuring stable, predictable combustion across a broad range of operational pressures.

VII. CONCLUSION

This review highlights the shifting paradigm in solid rocket propulsion as the aerospace industry seeks to transition from traditional Ammonium Perchlorate composite propellants to eco-friendly, chlorine-free alternatives. While traditional APCP formulations deliver dependable ballistics and robust mechanical integrity, their severe environmental impact makes the development of clean oxidizers an operational necessity. Among the candidates evaluated, Ammonium Dinitramide (ADN) delivers the highest thermodynamic performance, yielding specific impulse values that surpass APCP while ensuring completely non-toxic exhaust products. However, its high-pressure sensitivity and hygroscopic nature require advanced encapsulation and co-crystallization strategies before it can be deployed at scale.

Phase-Stabilized Ammonium Nitrate (PSAN) offers an exceptionally low-cost, stable, and clean alternative, though its lower baseline specific impulse requires the integration of energetic binders like HTPE and targeted transition-metal catalysts to achieve practical burning rates. Furthermore, resolving core operational risks—including acoustic combustion instability, multi-phase slag formation, and viscoelastic grain cracking—demands a design approach that integrates advanced finite element structural modeling with innovative manufacturing techniques like additive manufacturing. By combining optimized internal grain geometries with energetic green formulations, next-generation solid rocket motors can achieve high ballistic efficiency while meeting stringent modern safety and environmental standards.

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